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Chromium Redox on the Charging of Li-air Batteries

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Global warming due to greenhouse gas emission from large and rather inefficient usage of hydrocarbon fuel for energy production and transportation is an undeniable grand challenge of the century. Steps to electrify transportation can both provide efficiency boost in usage of traditional fossil fuels and allow flexibility in energy sources from coal to natural gas to renewables. Li-air (Li-O_2) batteries promise to provide energy densities upwards of three times that of current state of the Li-ion batteries utilized in emission-free electric vehicles (EV). Reducing the energy loss associated with Li_2O_2 electrochemical oxidation is paramount toward the development of efficient rechargeable lithium-oxygen (Li-O_2) batteries for practical use. While $LaCrO_3$ is inactive for oxygen evolution upon water oxidation in alkaline solution, it is found to have excellent catalytic effect towards Li_2O_2 oxidation. Further exploring Cr-based catalysts showed that Cr nanoparticles (Cr NP) with an average particle size of 40 nm, having oxidized surfaces, had comparable surface area activities to $LaCrO_3$ and mass activities comparable to noble metals Pt and Ru. Unlike Pt/C and Ru/C that promote electrolyte oxidation in addition to Li_2O_2 oxidation, no evidence of enhanced electrolyte oxidation was found having Cr NP relative to Vulcan carbon. X-ray absorption spectroscopy at the O K and Cr L-edge revealed a redox process of $Cr^{3+} \leftrightarrow Cr^{6+}$ on the surface of Cr NP upon Li_2O_2 oxidation, which might be responsible for the enhanced oxidation kinetics of Li_2O_2 and the reduced charging voltages of Li-O_2 batteries. This catalytic process is much unlike the traditional surface physisorption route encountered for oxygen evolution in aqueous media.